treatment with water for successive periods, gave decreasing values for the ratio of the iodine to the hydrogen equivalent.

The results of these experiments, though in themselves somewhat inconclusive, are worth recording, since they indicate that the reactions between boric acid and magnesium are by no means simple ones, and that further study of them may lead to the discovery of new compounds of magnesium and boron, of magnesium, boron, and oxygen, and also of new compounds of boron, oxygen, and hydrogen. This is a field of research which has not yet been explored, and we propose to continue our investigations upon the earliest opportunity.

A Chemically Active Modification of Nitrogen, Produced by the Electric Discharge.—IV*.

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§ 1. *General.*

The properties of active nitrogen have been described throughout on the assumption that it is to be classed with other chemical substances, and that its reversion to ordinary nitrogen is to be regarded simply as a chemical reaction, as one would regard the change of ozone to oxygen, or of red to ordinary phosphorus. I see no reason to abandon this position. There are, however, some circumstances not at first sight falling in very naturally with it. One of these is the acceleration of the change by cooling,† a phenomenon without parallel in any recognised reaction. Another is the development of many of the bands of the nitrogen spectrum.‡ This spectrum has never been produced by any other purely chemical process, but (apart from active nitrogen) is only observed when an electric current is actually passing through the gas at the moment of observation. Lastly, the ionisation associated with a stream of glowing nitrogen has suggested serious doubts whether its chemical peculiarities are really due to the presence of a definite chemical substance in the ordinary sense, or to some unexplained survival of

* I, 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 219; II, *ibid.*, 1911, vol. 86, p. 56; III, *ibid.*, 1912, vol. 86, p. 262.

† III, p. 263.

‡ 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 377.

the conditions of the disruptive discharge. Evidence will be brought forward in this paper which is considered to be entirely in favour of the former alternative.

§ 2. *Energy of Active Nitrogen.*

These considerations have made it important to determine whether the energy emitted by active nitrogen in reverting to ordinary nitrogen is comparable with that liberated in other chemical changes. The experiments to be described answer this question in the affirmative.

The general plan of experiment is to compare the energy given out by a definite stream of active nitrogen when allowed to revert to the ordinary kind, with the energy given out when the same stream reacts completely with nitric oxide. It is plain that this enables us to compare the energy of active nitrogen with that given out by an equivalent quantity of nitric oxide in the reaction. The latter is known from established calorimetric data. I have only carried out this experiment in a semi-quantitative manner. The time is scarcely ripe for attempting more.

A stream of nitrogen passes, first through a capillary tube of suitable dimensions, to regulate the flow,* then through a low-pressure discharge tube, to change it to the active condition; next through a thin-walled tube, in which it loses the heat acquired in the discharge,† and is approximately cooled to room temperature.

The active gas is then delivered into the tube *a* (fig. 1), vacuum-jacketed

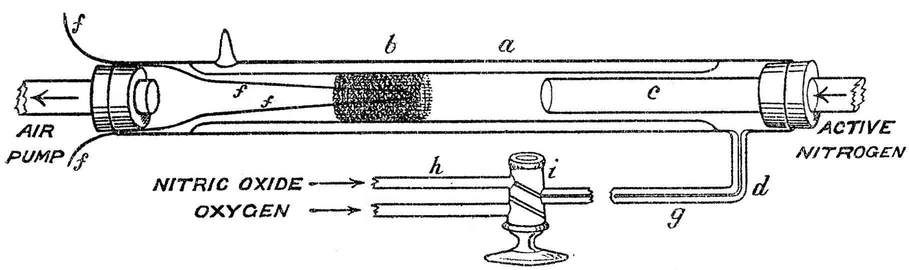

Fig. 1.

and silvered for heat insulation, by the jet *c*. In the course of its passage along *a* towards the air pump it partly goes back to ordinary nitrogen, with

* This was preferred to the use of a lubricated stopcock, as securing definiteness and constancy in the conditions.

† There is a certain want of definiteness about the initial temperature of the gas stream, for its internal energy is constantly being liberated all along its path. An experiment was made in which thermo-couples were introduced into the gas, up-stream and down-stream of an oxidised copper gauze plug, in which the internal energy was liberated. The initial temperature was 25° C.; the final temperature 60°.

rise of temperature. At *b* it comes in contact with a roll of oxidised copper gauze, where the decomposition is completed by a surface action.* The gauze accordingly becomes heated, and the rise of temperature is measured by a thermocouple enclosed in it, with leads, *f*, *f*, to a galvanometer outside.

When nitric oxide is led into the nitrogen stream by *d*, combination occurs, the characteristic flame being developed at the mouth of the jet *c*. If the two currents of gas are suitably adjusted the flame can be made to end short of the gauze plug. This adjustment is best done in preliminary experiments, without a silvered vacuum jacket.

Under these conditions it is observed that a notable rise of temperature occurs at the plug when nitric acid is admitted. This shows that the energy of active nitrogen is comparable with that of nitric oxide, for, when equivalent quantities of these substances react, the rise of temperature of the gas stream is notably greater than when the active nitrogen decomposes by itself.

To make the experiment definite, a precaution is necessary. The air-pump used to draw the gases along has a limited intake, and when the nitric oxide stream is admitted, an increase in the pressure of the discharge tube necessarily results. This alters the character of the discharge, and hence the percentage of active gas in the nitrogen stream and the rise of temperature resulting from its destruction. This source of uncertainty is eliminated by always allowing a tributary stream of gas to flow in, either nitric oxide or, alternatively, an equal stream of oxygen. The latter does not act chemically on active nitrogen, though hastening its decay, apparently by a catalytic action analogous to that of copper oxide.† Thus it assists the action of the oxidised gauze, and helps to secure destruction of all active nitrogen.

The oxygen stream has the further advantage of bringing the total gas stream up to nearly the same thermal capacity as it has when the nitric oxide is flowing, for oxygen and nitric oxide have about the same specific heat. Thus a given rise of temperature of the stream indicates the same energy given to it in each case. The oxygen and nitric oxide streams are made equal by using the same capillary tube *g* to regulate the admission of each. Their viscosities are appreciably the same. A two-way stopcock *h* serves to change over from one to the other.

A large number of experiments were made, and it was always found that admission of nitric oxide caused the temperature of the thermocouple to rise, and that it fell again when oxygen was substituted. The ratio of temperatures depended very much on the precise arrangement of apparatus. When nitric oxide is admitted, most of the heat is liberated near where

* I, p. 226. † II, p. 56.

the gases mix. The hot stream has therefore more chance of losing heat before it gets to the gauze plug in which the thermocouple is embedded. When no nitric oxide is passing, the chief liberation of energy is by contact action at the surface of the plug, thus the heat loss is less than in the former case. This source of uncertainty tends to exaggerate the energy of active nitrogen compared with that of nitric oxide.

Under different experimental conditions the rise of temperature when nitric oxide was admitted varied between 1·2 and 1·8 times that obtained with nitrogen only. The conditions could not be kept very constant, and, owing to the considerable thermal capacity of the plug, each experiment took time. There was, however, invariably a definite rise of temperature when nitric oxide was admitted. Thus the main point is established that the energy of active nitrogen is of the same order of magnitude as that of an equivalent of other substances. Nitric oxide is highly endothermic, and the experiments make it probable that active nitrogen considerably exceeds it in this respect.

Experiments made with acetylene instead of nitric oxide gave similar results. Since, however, tarry substances of unknown calorimetric value are produced in this reaction* it would be less suited for an exact quantitative determination.

§ 3. *Ionisation attendant on the Decay of Active Nitrogen.*

The general features of this have already been described.† I now pass to a quantitative investigation of it.

Some precautions necessary in experiments of this kind will first be described. Great trouble is experienced from the tendency to stray electric discharges from the induction coil used to generate active nitrogen. These discharges pass from the electrodes of the vacuum tube to those of the testing vessel, and disturb the electrical conditions there, so that the galvanometer behaves quite erratically. To avoid them, the coil, Leyden jar, and discharge tube must be enclosed in a box (*a*, fig. 2) lined with tinfoil, which is earthed *via* the gaspipes. From the discharge tube, *b*, the gas is led out by a tube which passes through a hole in the side of the box. This tube should be locally constricted to 2 or 3 mm. internal diameter where it passes through the hole. This precaution is important. The electrode *c* nearest the exit should be in connection with the box, and a supplementary electrode *e* should be provided in metallic contact with both, as shown. A small fraction of the current from the electrode *d* fails to flow away by *c*, but escapes past it, and gets to earth by any channel

* I, p. 228. † II, p. 60.

available. The supplementary electrode *e* provides the channel required, and prevents this residual discharge passing to earth *via* the electrodes of the ionisation chamber. The constriction of the tube assists towards the same object.

After leaving the discharge tube the gas passes to the ionisation chamber *f*, and flows between the parallel plate electrodes *h*, 10 mm. apart.

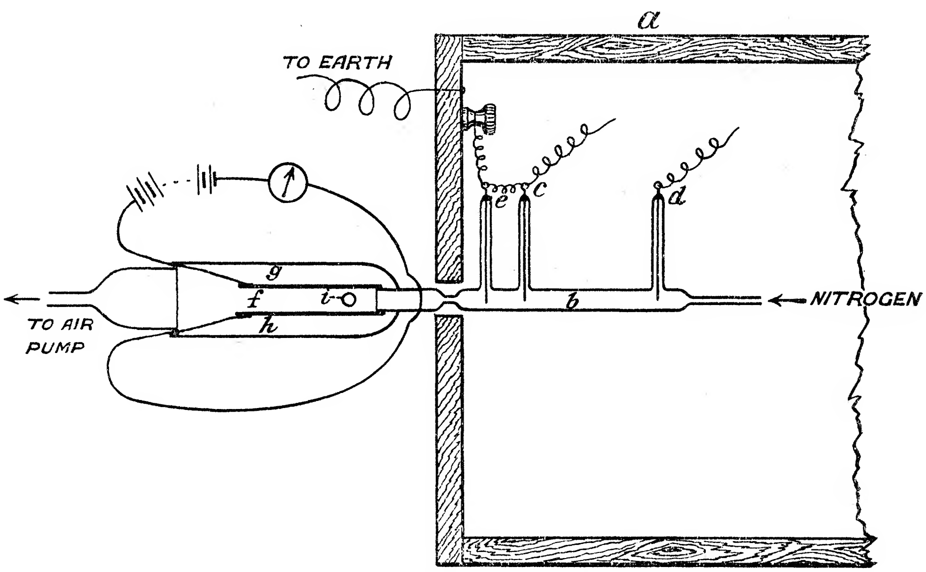

Fig. 2.

These are in circuit with a galvanometer and a battery of small storage cells. The glow decays completely in its course along this vessel.

The first point was to examine the relation between current and E.M.F. It was found that with a bright active nitrogen glow between the plates at low pressure saturation could not be obtained, the current continually increasing with the E.M.F. until discharge occurred between the testing electrodes.

Probably ionisation by collision occurred under these conditions. When, however, the pressure of gas in the ionisation vessel was higher, and the original generating discharge not too strong, saturation was obtained. The following set of measurements, between plane electrodes 1 cm. apart, may be given as an example :—

E.M.F. volts.	Current. microampères.	E.M.F. volts.	Current. microampères.
80	14	320	18
160	18	400	19
240	18	480	19

No effect whatever on the intensity of the luminous glow was observed when this saturating field was applied. This is in accordance with previous experiments,* and affords conclusive evidence that the glow is not due to the presence of ions—for it is unaffected by removing them.

The next point was to obtain a quantitative relation between the amount of active nitrogen entering the ionisation vessel per second and the current carried. For this purpose the nitric oxide method of estimation was used,† the reaction being allowed to take place in the same vessel as was used for ionisation tests. A suitably regulated current of nitric oxide was admitted through a capillary tube to the ionisation chamber. The tube by which it enters is seen in section at *i*. As in the heat experiments, previously described, the current of nitric oxide could be replaced by an equal current of nitrogen‡ so as to avoid disturbing the pressure conditions.

When the nitrogen glow was developed between the electrodes, the ionisation current was about 20 microampères. On admitting nitric oxide the nitrogen glow was replaced by the nitrogen peroxide flame§ with continuous spectrum, and the current fell to about 1 microampère. It appears at once, therefore, that the amount of ionisation developed by a given stream of active nitrogen depends entirely on the particular fate which it meets with, and is not a fixed property of the stream. Many more ions are produced if it goes back to ordinary nitrogen than if it reacts with nitric oxide.

Confining our attention to the case of nitrogen alone, it was found that the current carried was infinitesimal in comparison with that which would be conveyed by the same mass of nitrogen according to the electrochemical equivalent. Thus, in one experiment, the stream of active nitrogen passing was such as to yield in 15 minutes 26·4 mgrm. of the blue liquid N_2O_3. This indicates $26{\cdot}4 \times 14/76 = 4{\cdot}87$ mgrm. of active nitrogen in 15 minutes, or 19·5 mgrm. per hour.

Now, if every atom of nitrogen in this contributed one positive and one negative ion, the saturation current would be $37{\cdot}1 \times 10^3$ microampères. This is about 1,500 times greater than the saturation current actually observed, which was 24·9 microampères. Thus, only one nitrogen atom in 1,500 of those concerned gets ionised.

In the above experiment every precaution was taken to guard against error in the chemical determination. Blank tests of 15 minutes' duration, without a discharge to make the nitrogen stream active, were made before and after the actual experiment, but no nitrogen trioxide could be collected.

* II, p. 61.

† II, p. 57.

‡ Taken off by a branch tube from the supply of nitrogen to the original discharge tube.

§ II, p. 57.

As already mentioned, the ionisation associated with a stream of glowing nitrogen has suggested doubts whether its chemical peculiarities are really due to the presence of a definite chemical substance in the ordinary sense, or to some unexplained survival of the conditions of the disruptive discharge. I think the latter possibility must now be dismissed; for it is clear that the ions are so few, compared with the number of atoms concerned in the chemical action, that we can only regard them as a by-product of the processes which are going on.

The ions formed in the reversion of active nitrogen may be compared with those formed in the glow oxidation of phosphorus, which are also very few compared with the number of reacting atoms. It is significant that each of these actions is accompanied by luminosity.

Is it not possible that the ionisation is the direct consequence of the luminosity? It is known that ionisation is produced by light in the far ultra-violet region of the spectrum—the Schumann region.* Whether the active nitrogen glow extends to this region, and, if so, with what intensity, is not known, though the determination would not be difficult to an experimenter who possessed the very special appliances necessary. It may be objected that the ionisation observed in the reversion of active nitrogen, though small compared with the number of atoms concerned, is still enormous compared with any observed to be produced by ultra-violet light. But nitrogen luminosity, acting on nitrogen atoms, may produce special effects of resonance. The subject is too speculative to pursue further, beyond the remark that this hypothesis is consistent with the change of ionisation which generally results when other chemical substances are added, modifying the nature of the glow.†

§ 4. *Effect of Temperature.*

In former experiments it was shown that the nitrogen glow could be brilliant at $-180°$ C., and that it was of shorter duration than would otherwise have been the case. I find that these observations have been in part anticipated by C. C. Trowbridge.‡ His experiments were not, however, designed or interpreted with definite reference to the chemical nature either of the original gas present or of the change occurring.

As before mentioned,§ local cooling causes concentration of the gas in the part of the vessel cooled, and proof is required that this is not the effective cause of the brightening. Such proof was found in the shortened duration of the glow when the whole vessel was suddenly plunged in liquid air. It

* Hughes, 'Camb. Phil. Soc.,' 1910, vol. 15, p. 483.

† II, p. 60.

‡ 'Phys. Rev.,' 1906, vol. 23, p. 296.

§ III, p. 262.

would, however, be satisfactory to obtain in addition definite evidence that the luminosity is increased in intensity as well as shortened in duration. There is difficulty—not perhaps insurmountable—in getting this when the vessel is cooled all over, for we have no convenient standard of comparison for the luminosity. I returned, therefore, to the method of local cooling, compensating for the concentration thus caused by looking through a smaller thickness of luminous gas.

The evidence already given* justifies the supposition that the change is a bimolecular one, occurring at a rate proportional, *ceteris paribus*, to the number of collisions per second between molecules of active nitrogen. If the gas is locally cooled in a closed vessel, with equality of pressure throughout, the number of collisions at any part of it is, according to the kinetic theory, proportional jointly to the square of the concentration and to the molecular velocity. The former factor varies as t^{-2}, the latter as $t^{\frac{1}{2}}$, where t is the absolute temperature. Upon the whole, therefore, the number of collisions per second in various parts of the vessel varies as $t^{-\frac{3}{2}}$. If one part of the vessel is at room temperature (20° C.), and another in liquid air, the molecular collisions in the latter will be more numerous in the ratio 5·6 : 1.

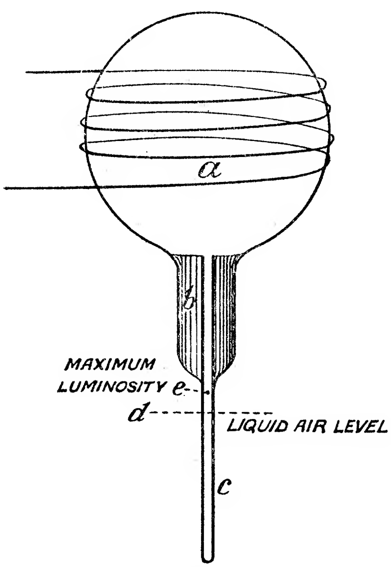

Fig. 3.

A bulb of 300 c.c. capacity (*a*, fig. 3) had a neck *b* 19 mm. in internal diameter. A narrow tube *c*, 3·4 mm. diameter, was sealed on to it. These diameters are in the above ratio 5·6 : 1. The bulb was exhausted and charged with nitrogen to a suitable pressure, so as to glow brightly after excitation by the electrodeless discharge.

The narrow neck was immersed in liquid air up to *d*, and, when the temperature had settled down, the bulb was excited. The afterglow was seen to be intrinsically much brighter—four or five times perhaps—in *c* than in the broad neck *b*. It was found convenient to make *b* opaque with black varnish outside, except for a narrow strip of the same width as *c*. This made comparison easier.

Maximum brilliancy was observed at a point *e* somewhat above the level

* III, p. 267.

of the liquid air, though still in the narrow tube. This may have been due to the restricted access of fresh supplies of active nitrogen to the narrow tube, where it was being used up so fast. Thus an inadequate supply would reach the fully cooled part of the tube. So far as this cause may have acted, it makes the experiment not less but more significant. At least as many molecular collisions were occurring in the deep stratum of luminosity in *b* as in the shallow stratum at *e*. But *e* was much the brightest.

I wish now to enter more speculative ground. There is considerable reason for thinking that active nitrogen is simply monatomic nitrogen. Indeed the choice seems to lie between that and triatomic,* unless indeed we are prepared to consider the possibility of a very complex molecule. Let us assume the monatomic view as a working hypothesis. It may then be assumed that the ratio of specific heats (the direct determination of which presents insuperable difficulties) has the value 1·67 found in other monatomic gases.†

If this is so, then, as Clausius first pointed out, the whole energy put into the gas by raising its temperature goes into increasing the translational energy of the molecules. There is none left to increase their internal energy, whether rotational or otherwise.‡

No other chemical action has been studied in which the reacting systems are monatomic. The reversion of active nitrogen is the only chemical change we know of which is not accelerated by heating, and the only one in which the internal energy of the reacting systems is not increased by the same cause. Is this an accident?

When a non-explosive chemical change occurs throughout the volume of a gas or a gaseous mixture, it is certain that the collisions which result in chemical combination are a very small fraction of the total number. The great change in the velocity of reaction which usually accompanies a rise of temperature affords proof of this.

What is the peculiarity of the molecules which make successful collisions? It is usually supposed, so far as I know, that they are molecules of exceptional translational velocity. This would explain the great effect which a moderate rise of temperature produces on the velocity of reaction, for rise of temperature increases very greatly the number of molecules having velocities in excess of

* III, p. 267.

† As regards mercury vapour, no objection will be taken to this; but as regards the helium group of gases, it may be objected that we rely on the ratio of specific heats to determine monatomicity, and that the argument cannot be used conversely. Originally this objection would have been valid. Now, however, many facts in radioactivity, intelligible on the hypothesis that helium is monatomic, would no longer be so if we abandoned that hypothesis. There is also evidence from the periodic law.

‡ See, for instance, O. E. Meyer's 'Kinetic Theory of Gases,' p. 118.

some assigned value large enough to make the molecules in question exceptional.

But when we consider the reversion of active nitrogen this theory fails entirely. For increase in the translational velocity of the molecules, so far from increasing the number of successful collisions, positively diminishes it. I infer, therefore, that in this case, and probably in others also, it is not the exceptional violence of the collision which makes it result in combination. Indeed, it is difficult to see, from a mechanical point of view, why it should do so. If we permit ourselves the analogy of indiarubber balls coated with some adhesive substance, the more violent the collision, the less likely it is that the balls will permanently adhere.

We are reduced, then, to assume that a successful collision (*i.e.*, one that results in chemical union) is mainly conditioned by something internal to the molecule. As the upshot of these considerations the following theory is suggested.

High translational velocity of the molecules is in itself unfavourable to chemical union. And if, as in the case of monatomic nitrogen, the whole energy of a higher temperature goes to increasing this velocity, the rate of chemical transformation will be diminished by heat. In ordinary cases, however, when the reacting molecules are more than monatomic, the increase of internal energy more than outweighs the unfavourable influence of an increase in translational energy, and, upon the whole, a rapid increase in the rate of combination results.

It is not within the scope of this theory to explain how an increase of internal energy, probably rotational, can facilitate chemical union of diatomic or polyatomic systems. A crude suggestion, indicating how this might be possible, would be that a rapidly rotating system, internally strained by centrifugal force, is readier to break up, preparatory to entering on a new configuration.

§ 5. *Summary.*

(1) Active nitrogen is a highly endothermic body, but its energy is of the same order of magnitude as that of other chemical substances.

(2) In the reversion of active to ordinary nitrogen, the number of atoms ionised is a very small fraction of the whole number concerned in the change. The ionisation is a subordinate effect, and may be due to light of very short wave-length emitted in the reaction.

(3) Additional experiments are described to prove that the change of active nitrogen is more rapid at low temperatures. This is thought to be connected with the monatomic character of the molecule, and to throw light on the connection between temperature and velocity of reaction in other cases.